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The Effect on Soil Fertility of Repeated Applications of Pesticides over 20 Years

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Abstract: Concern has been expressed that repeated use of pesticides may be leading to accumulation of residues in soil and to damaging effects on the environment. A long-term experiment, known as the Chemical Reference Plots, was started in 1974 on a silty clay loam soil at Rothamsted in which plots received applications of up to five pesticides (aldicarb, benomyl, chlorfenvinphos, glyphosate and chlorotoluron or triadimefon), each plot receiving the same treatment annually for up to 20 years. Spring barley was grown each year, and its yield was taken as an indicator of soil fertility. The glyphosate and triadimefon were applied to the autumn stubble prior to ploughing from growing seasons 1980 and 1982 respectively, chlorotoluron was sprayed pre-emergence (1974 and 1976 only) and the other compounds were incorporated into the soil in spring immediately before sowing (1974–1993 inclusive). No deleterious effects on crop productivity were observed from these pesticide applications, and no differences could be found in microbial processes in soils sampled in April 1992 save for a small increase in the amount of microbial-biomass carbon in plots receiving aldicarb. No pesticide residues could be detected in soil taken in August 1994, 17 months after the last experimental treatment. In laboratory incubations using these same soil samples, the degradation of aldicarb residues was greatly enhanced in plots that had received aldicarb for 20 years, whereas degradation rates of benomyl, chlorfenvinphos and triadimefon residues were not influenced by the treatment history.

Key words: soil fertility, microbial populations, aldicarb, benomyl, chlorfenvinphos, chlorotoluron, glyphosate, triadimefon, spring barley

1 INTRODUCTION

The use of pesticides has come in for increasing criticism in recent years, with aspects of public concern including both the possible accumulation of pesticide residues in soil following repeated applications to crops and deleterious effects on soil micro-organisms with adverse long-term consequences for soil fertility. The prime indication of soil fertility is taken as the ability to produce crops in a sustainable manner, but other processes such as the maintenance of organic matter content and of microbial populations are also factors.[1]

Most crops in the UK receive pesticides, and indeed the use of pesticides has been widespread here and in the rest of the developed world for the past 50 years. As an example, in the 1980s, pesticide usage in England and Wales averaged around 28 000 tonnes of active ingredient per year on arable crops. Of this, typically 73% was herbicides and desiccants, 17% fungicides, 7% plant growth regulators and 3% insecticides.[2,3] Though usage is no less intensive, the weight of applied pesticides is now declining, primarily due to the introduction of new compounds (especially herbicides) with higher activity.

Short-term problems with pesticides in soils are occasionally observed. One such example is the carry-over of herbicide residues,[4] which occurs particularly after dry summers because degradation of pesticides is

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much slower in dry soil. This difficulty can usually be overcome by mixing the topsoil to dilute the herbicide residues and so reduce the risk of phytotoxicity to following crops. Changing the use of areas such as orchards, where relatively persistent and non-selective herbicides such as simazine and bromacil are used repeatedly to maintain fallow strips, can be difficult, and it may be several years before arable crops can be grown successfully on such sites.[5] Orchards and vineyards also receive repeated applications of fungicides, and some of these, such as copper salts (as Bordeaux mixture) and benzimidazoles (e.g. benomyl), can greatly reduce worm populations in soil.[6]

Were long-term problems to be occurring, the widespread and repeated use of pesticides should give opportunities for such problems to be readily observed. However this has not been so. Nonetheless subtle deleterious effects could be occurring, and such effects, for example on crop yield, could be masked by improvements in crop varieties and agronomic practices.

Few experiments have been set up to assess possible deleterious effects on soil fertility caused by repeated applications of pesticides over many years. At the now closed Weed Research Organisation, Fryer and coworkers[7–9] observed that annual applications of individual herbicides (MCPA, tri-allate, simazine and linuron) at commercial rates over 16 years from 1963 did not reduce crop yields nor have any measurable effect on the nutritional status of the soil. Monitoring of the persistence of the compounds in this experiment, and in laboratory incubations[10] using soil from an adjacent area treated nine times with simazine over five years, showed that there was no build-up of herbicide residues despite the repeated applications.

On a Black Chernozem soil in Saskatchewan, Canada, plots of spring wheat have received annual applications of the herbicides 2,4-D (since 1947) and MCPA (since 1953). Reporting on the period to 1988, Smith *et al.*[11] found no ecologically significant effects on selected soil biochemical processes, nor had the herbicides interfered with the normal cycling of carbon, nitrogen or phosphorus. No herbicide residues could be found in soil, and indeed breakdown rates were shown in laboratory tests to be enhanced in soil from the plots receiving the herbicides, indicating microbiological adaptation. No adverse effects on crop productivity were observed.

To address this whole question with a wider range of pesticides, a long-term field experiment known as the Chemical Reference Plots was set up at Rothamsted in 1973. Individual plots received annual applications of up to five pesticides, each plot receiving the same treatment for up to 20 years (1974–1993). Not all these chosen pesticides would normally be applied to cereals, nor applied directly to soil as was done here; the intention was to choose commonly used pesticides spanning a range of important pesticide classes, and to use them at rates representing the highest likely to be used so as to provide a severe test for possible effects on soil fertility. Spring barley was grown each year, and its yield was monitored as an assessment of soil fertility; this crop was chosen as being typical for this situation and one that could be grown continuously without encountering severe disease or pest problems. Other parameters, such as breakdown rates of the pesticides, effects on microbial populations and effects on nematode populations, were assessed towards the end of the experiment, together with measurement of pesticide residues in the topsoil. This paper reports on the effects of these 20 years of pesticide treatments; the experiment is being continued for five years (1994–1998) without further pesticide applications in order to assess residual effects.

2 MATERIALS AND METHODS

2.1 Field plots

2.1.1 Plot treatments

The Chemical Reference Plots (32 in total) are a 2^5 factorial design with a single replicate of each treatment combination, fully randomised. Each plot is $4{\cdot}06 \times 4{\cdot}57$ m^2, in four blocks of eight plots, with plots located by permanent markers. Neighbouring plots were separated by paths of widths 0·9 m between the eight plots within a block and of width 2·5 m between the four blocks. Paths and surrounds were planted as the plots. The soil is a neutral silty clay loam with approximately 2·8% organic matter, and containing 27·3% water (by weight) at field capacity.

Each plot was intended to receive the same combination of up to five pesticides every year for 20 years, starting in 1974 and ending in 1993. The treatments were no pesticides (one plot), a single pesticide (five plots) and all combinations of two, three, four and five pesticides (10, 10, 5 and 1 plot respectively). The first treatments were applied in spring 1974. The carbamoyloxime insecticide/nematicide aldicarb and the organophosphorus insecticide chlorfenvinphos (6 and 2 kg AI ha^{-1} respectively, both as 100 g AI kg^{-1} granules) and the benzimidazole fungicide benomyl (4 kg AI ha^{-1}, as a wettable powder) were applied to the seedbed by hand (by pepper pot and watering can respectively) and incorporated by harrowing (usually with a Roterra); immediately afterwards, non-dressed seed of spring barley was sown. All other treatments were applied by conventional tractor-mounted sprayers. From 1974 to 1980, the phenylurea herbicide chlorotoluron (2 kg AI ha^{-1}, as an emulsifiable concentrate) was intended to be sprayed pre-emergence, but weather conditions made it difficult to apply this treatment every year (only applied 1974 and 1976); consequently this

treatment was replaced by the triazole fungicide triadimefon (0·25 kg AI ha^{-1}, as a wettable powder) applied to the stubbles (first applied autumn 1981, for the 1982 growing season). From autumn 1979, a herbicidal glyphosate spray (target rate 1·5 kg AI ha^{-1}, formulated as the isopropylamine salt; see Table 1 for actual rates) was introduced as the fifth treatment and also applied to the stubbles, and subsequent ploughing incorporated these two autumn-applied compounds. Dates of these pesticide applications are given in Table 1; the last autumn and spring treatments of the 20-year regime were applied on 28 September 1992 and 9 March 1993 respectively.

The spring barley (*Hordeum vulgare* L., cvs given in Table 1) received standard farm practice with regard to agronomic treatments. In particular, it should be noted that *all* plots received an application of herbicide (Table 1) at the recommended commercial rates to the growing crop in May/June in all years save 1976 and 1981, and additionally tridemorph fungicide was applied for mildew control in 1980 and 1987; these treatments were necessary to give adequate and uniform control of weeds and diseases in order to obtain meaningful barley yields. In some years, levels of aphids and mildew were assessed on all plots throughout the growing season to see if these were influenced by the treatments. The barley was harvested by a combine harvester, and yields were assessed annually from a strip of 17 rows × 4·57 m (approximately half the plot area).

2.1.2 Statistical analysis of yields

The experiment was a single replicate of a 2^5 design in the last 12 years. In the first eight years, when only four treatments were applied, it comprised two replicates of a 2^4 design, fully randomised. Analyses of variance were used to interpret the yields of grain. The three- and four-factor interactions were examined over this first period, and were never significant. Consequently the analysis for the last 12 years assumed that these higher interactions were negligible, and they were used to estimate the experimental error in the absence of true replication. Analyses were done on yields averaged over the 20 years of the experiment, and also in five four-year periods corresponding approximately to the treatment changes.

2.2 Pesticide standards

Pesticides used as analytical standards and in the incubation experiments were received as gifts of analytical grade. Benomyl is very rapidly broken down in soil to carbendazim, which is the main active component, and so carbendazim was utilised in the laboratory incubations.

The synthesis and purification of [^{14}C]aldicarb, labelled in the methyl group of the carbamoyl moiety and used at a specific activity of 3·3 MBq $mmol^{-1}$, have been described previously.[12]

2.3 Soil sampling and pesticide incubations

Soil samples were taken on 1 August 1994, 22 and 17 months after the last autumn and spring applications, respectively, of the pesticides, to a depth of 15 cm. Plots sampled were the control, those receiving repeated treatments of a single pesticide (aldicarb, benomyl, chlorfenvinphos or triadimefon) and that receiving all the pesticides annually. Incubations were not done with glyphosate as this compound is known not to be persistent.[13] Of the five treatment pesticides used in the latter part of the experiment, four (benomyl, chlorfenvinphos, glyphosate and triadimefon) and their active breakdown products considered below are quite strongly sorbed to soil, and so their movement or influence on processes below the topsoil was considered likely to be negligible. Aldicarb and its oxidation products are weakly sorbed, but movement of spring applications would be slight, especially in the last five years of the experiment when the breakdown of aldicarb was accelerated; accordingly it was again considered justifiable to examine processes only in the topsoil. Samples were taken randomly from approximately twenty positions across a plot using a trowel, and then composited (total weight approximately 4 kg), thoroughly mixed and sieved (without drying) to 4 mm. After removal of samples to be analysed for pesticide residues, the remainder was wetted up to 80% field capacity and allowed to equilibrate for four days prior to setting up the incubation experiments. Initial incubations with benomyl (applied as carbendazim)[14] were very variable, and these tests were repeated with soil sampled in April 1995, i.e. 25 months after the last benomyl treatment.

Each pesticide was incubated in soils from three plots (control and the plots receiving that pesticide either singly or in combination with all the other pesticides). For the incubations, samples of the prepared soils (20 g) in screw-capped 100-ml glass bottles were treated with the pesticide in methanol (0·1 ml), the bottles being left uncapped for 30 min to allow the methanol to evaporate. The bottles were then weighed, loosely capped and incubated at 15°C in the dark; water was added occasionally as necessary to maintain the moisture content. The application rates mirrored the field treatments: for the chemicals incorporated into the plots, rates were 3·0 $\mu g\ g^{-1}$ soil for [^{14}C]aldicarb, 1·32 $\mu g\ g^{-1}$ for carbendazim (equivalent to 2·0 $\mu g\ g^{-1}$ for benomyl) and 1·0 $\mu g\ g^{-1}$ for chlorfenvinphos; for triadimefon, which was applied to stubbles at a low rate and ploughed in, less mixing would occur and so a concentration of 1·0 $\mu g\ g^{-1}$ was used. Duplicate sample bottles were removed for analysis at the start of the incubations, and at appropriate intervals thereafter.

TABLE 1
Experimental Details for the Chemical Reference Plots, 1974–1993

Growing season	*Barley variety*	*Experimental pesticides*[a] *Date applied*		*Ald.*	*Ben.*	*Chlorf.*	*C'tol.*	*Gly.*[b]	*Tri.*	*Basal herbicides* *Date applied*	*Compounds*
1974	Julia	—	28 Mar. '74							21 May '74	Dicamba, mecoprop, MCPA
1975	Julia	—	22 Apr. '75							6 June '75	Dicamba, mecoprop, MCPA
1976	Julia	—	9 Mar. '76							—	
1977	Julia	—	10 Mar. '77							23 May '77	Dicamba, mecoprop, MCPA
1978	Porthos	—	8 Mar. '78							10 May '78	Dicamba, mecoprop, MCPA
1979	Porthos	—	6 Apr. '79							30 May '79	Mecoprop, bromoxynil, ioxynil
1980	Georgie	13 Sept. '79	5 Mar. '80							11 May '80[c]	Dicamba, mecoprop, MCPA
1981	Triumph	25 Sept. '80	8 Apr. '81							—	
1982	Triumph	22 Sept (26 Nov.) '81	25 Mar. '82							18 May '82	Dicamba, mecoprop, MCPA
1983	Triumph	2 Sept. '82	9 Mar. '83							16 May '83	Dicamba, mecoprop, MCPA
1984	Triumph	1 Nov. '83	2 Apr. '84							31 May '84	Dicamba, mecoprop, MCPA
1985	Klaxon	26 Sept. (17 Oct.) '84	19 Mar. '85							10 May '85	Mecoprop, bromoxynil, ioxynil
1986	Klaxon	27 Sept. (11 Oct.) '85	29 Apr. '86							12 June '86	Bentazone, dichlorprop, MCPA
1987	Klaxon	22 Sept. (13 Oct.) '86	19 Mar. '87							6 May '87[c]	Bentazone, dichlorprop, MCPA
1988	Doublet	5 Oct. (30 Oct.) '87	7 Apr. '88							5 May '88	Bentazone, dichlorprop, MCPA
1989	Klaxon	10 Aug. '88	31 Mar. '89							9 May '89	Dichlorprop, MCPA
1990	Klaxon	3 Oct. '89	13 Mar. '90							23 May '90	Bromoxynil, ioxynil, mecoprop
1991	Klaxon	28 Sept. '90	8 Apr. '91							16 June '91	Fluroxypyr
1992	Alexis	6 Nov. '91	11 Mar. '92							20 May '92	Bromoxynil, clopyralid, mecoprop-P
1993	Alexis	28 Sept. 92	9 Mar. '93							28 May '93	Fluroxypyr, metsulfuron-methyl

[a] Ald. = aldicarb, Ben. = benomyl, Chlorf. = chlorfenvinphos, C'tol. = chlorotoluron, Gly. = glyphosate, Tri. = triadimefon; filled lines indicate years of treatment. Glyphosate and triadimefon (date of application of triadimefon given in parenthesis when not applied on same day) were applied in autumn, the others in spring with chlorotoluron applied 2 April 1974 and 24 Mar. 1976 only.

[b] Application rates achieved were 1·4 kg ha^{-1} in growing seasons 1980–1985, 0·72 kg ha^{-1} in 1986, 0·54 kg ha^{-1} in 1987, 1·3 kg ha^{-1} in 1988 and 1·5 kg ha^{-1} over 1989–1993 (applications made in the autumn of the preceding year).

[c] The fungicide tridemorph was also applied in these two years, on 4 June 1980 and 6 May 1987.

2.4 Analytical methods

2.4.1 High-pressure liquid chromatography (HPLC)
The column was 20 cm × 4·6 mm ID, packed with 10 μm Spherisorb ODS, with 20-μl loop injection and solvent flow rate of 2·0 ml min^{-1}. Running solvents were acetonitrile + water (60 + 40 by volume) for chlorfenvinphos, acetonitrile + water (50 + 50 by volume) for triadimefon (and its transformation products, the two diastereoisomers of triadimenol) and acetonitrile + 0·1 M aqueous ammonium hydroxide (20 + 80 by volume) (in early work, acetonitrile + water (25 + 75 by volume) was used, but retention times with this mixture were less consistent) for carbendazim, with detection at wavelengths of 244, 223 and 286 nm respectively.

2.4.2 [^{14}C]Aldicarb and its oxidation products
Soil samples (20 g) were extracted with acetone (75 ml) in stoppered glass bottles (500-ml) by orbital shaking for 4 h. Two aliquots (each 15 ml) of the supernatant liquid were taken, one to measure total ^{14}C and the second for thin-layer chromatography to determine the components present; as the ^{14}C-label was in the methylcarbamoyl moiety, essentially all the extracted ^{14}C could be attributed to aldicarb and its two oxidation products, the sulfoxide and sulfone.

One aliquot was placed in a 20-ml scintillation vial, water (1·0 ml) added as a keeper and the acetone evaporated by forced draught in a fume hood; radioactivity was then assessed by adding Scintran Cocktail T (10 ml) and counting in a liquid scintillation counter (Kontron Betamatic V) for 20 min with quench correction by external standard. The efficacy of recovery from soil for aldicarb was 89·6%.

The second aliquot was evaporated just to dryness in a 50-ml round-bottomed flask on a rotary evaporator at a bath temperature not exceeding 30°C. The residue was transferred in a little acetone to a thin-layer chromatography plate divided into 1-cm-wide bands of silica gel 60F (Whatman, 250 μm layer with pre-absorbent strip) and developed with diethyl ether + acetone (4 + 1 by volume).[12] Peaks corresponding to aldicarb and its two oxidation products were identified using a Berthold linear analyser (counting time 20 min) and quantified by allocation of the total ^{14}C as determined above.

2.4.3 Chlorfenvinphos and triadimefon (including triadimenol)
Soil samples (20 g) were extracted with methanol (75 ml) in 100-ml screw-capped incubation bottles by end-to-end shaking for 4 h. An aliquot (25 ml) of the supernatant liquid was evaporated to dryness in a 50-ml round-bottomed flask on a rotary evaporator. The residue was dissolved by ultrasonification in the running solvent (1·0 ml) for analysis by (HPLC) (see Section 2.4.1). Recovery efficiencies were 89·0 and 94·5% for chlorfenvinphos and triadimefon respectively.

2.4.4 Carbendazim (including benomyl)
Soil samples (20 g) were extracted with acetone + 1 M aqueous ammonium chloride (1 + 1 by volume) in 100-ml screw-capped incubation bottles by end-to-end shaking for 4 h.[15] An aliquot (25 ml) of the supernatant liquid had the acetone removed using a rotary evaporator, and was then acidified with concentrated hydrochloric acid (two drops). This solution was extracted with ethyl acetate (2 × 15 ml), and the extract discarded. To the aqueous phase was then added 6·5 M sodium hydroxide (five drops), followed by extraction with ethyl acetate (2 × 15 ml) with these extracts being combined and evaporated to dryness as above. The residue was taken up in methanol + water + 30% ammonium hydroxide (100 + 100 + 1 by volume) (1·0 ml) for HPLC (see Section 2.4.1). Recovery efficiency was 63%.

2.5 Derivation of rate constants

The rate constants were estimated in models fitted by least squares using the Maximum Likelihood Program (MLP).[16] All processes were assumed to follow first-order kinetics. Carbendazim and chlorfenvinphos were assumed to be degraded directly to innocuous metabolites; aldicarb was taken to be sequentially oxidised to sulfoxide and then sulfone, with these three compounds being subject to other processes effecting loss of the methylcarbamoyl group; triadimefon was simultaneously reduced to the two triadimenol diastereoisomers (1*R*,2*S*; 1*S*,2*R* and 1*R*,2*R*; 1*S*,2*S*), these three compounds also being subject to other loss processes.

3 RESULTS

3.1 Crop yield and soil fertility

The mean yields over all plots in each of the years 1974–1993 are given in Table 2. The year-to-year fluctuations followed local trends and appeared to be due to the weather, especially the spring rainfall. The influences of the five main pesticide treatments, applied for between 12 and 20 years, are shown in Table 3, which compares the 16 plots repeatedly receiving a particular compound to the 16 plots not receiving it; for each compound, possible direct influences of the other applied pesticides balance out in this comparison. Aldicarb treatment increased yield slightly but significantly ($P < 0·01$), whilst the other compounds (benomyl, chlorfenvinphos, glyphosate and triadimefon) had no significant effect on yield ($P > 0·05$) over these long periods.

A further analysis was done utilising four-year periods to see if any trend in yields could be discerned

TABLE 2
Rainfall and Spring Barley Yields for the Chemical Reference Plots, 1974–1993

Growing season	Rainfall over growing season (mm)	Mean barley yield (tonne ha^{-1})
1974	211·1	6·17
1975	121·8	5·18
1976	115·9	3·96
1977	316·5	4·77
1978	363·1	4·94
1979	258·4	4·62
1980	316·6	4·73
1981	269·5	6·18
1982	250·7	5·20
1983	315·6	4·41
1984	178·8	5·14
1985	319·8	7·14
1986	225·7	5·97
1987	326·2	5·26
1988	243·4	4·29
1989	201·6	3·90
1990	110·7	4·45
1991	269·4	6·08
1992	309·3	5·12
1993	376·5	4·20

TABLE 3
Effect of Long-Term Pesticide Treatment on Yield of Spring Barley

Treatment[a]	Mean annual yield of barley (tonne ha^{-1})[b]	
	Untreated	Treated
Aldicarb	4·99	5·19
Benomyl	5·06	5·12
Chlorfenvinphos	5·1	5·08
Glyphosate	5·13	5·17
Triadimefon	5·05	5·14

[a] Plots treated annually with pesticides to 1993: aldicarb, benomyl, chlorfenvinphos (each over 20 years); glyphosate (14 years); triadimefon (12 years).
[b] Maximum standard error of difference was 0·05 tonne ha^{-1}.

(Fig. 1). Aldicarb increased yield in the first four four-year periods ($P < 0·01$ in the first and third period, $P < 0·1$ in the second and $P < 0·05$ in the fourth) but no measurable difference occurred in the fifth period. The other compounds generally showed no significant effect, except that benomyl ($P < 0·05$) and triadimefon ($P < 0·01$) in 1982–85 and glyphosate ($P < 0·05$) in 1990–93 increased yield.

Interactions between pairs of compounds were occasionally significant ($P < 0·05$), but such effects were inconsistent and no more frequent than would be expected by chance. Accordingly it is considered that two-way interactions were not important.

3.2 Pesticide residues in soil from the plots

The soil samples taken in August 1994, i.e. 17 to 22 months since the last treatments, were analysed for residues of the more persistent compounds (aldicarb and glyphosate[13] were omitted as they are rapidly broken down—see Section 3.3.4). None of the other three main pesticides could be detected in these soil samples; the

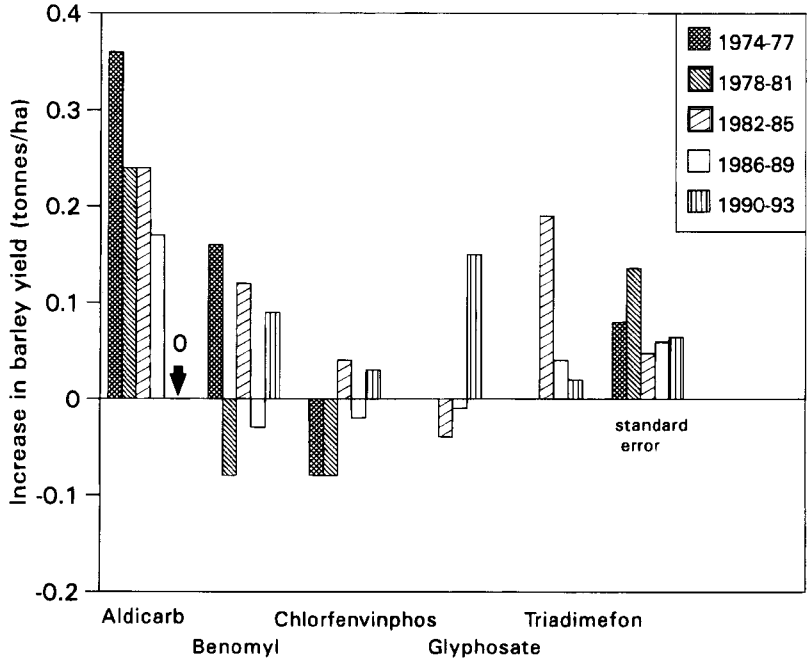

Fig. 1. Increases in barley yield, averaged over four-year periods, caused by repeated annual applications of pesticides (glyphosate and triadimefon only considered from 1982 onwards, see text).

detection limits were 0·05, 0·15 and 0·06 $\mu g\ g^{-1}$ soil for carbendazim, chlorfenvinphos and (1*R*,2*S*; 1*S*,2*R*)-triadimenol (the major persisting transformation product of triadimefon) respectively, corresponding to <0·2, <0·8 and <3% respectively of the total amounts applied. Thus no accumulation of these pesticides had occurred.

3.3 Degradation rates of the pesticides in laboratory tests in soil

3.3.1 Chlorfenvinphos

No difference was observed in the breakdown rates of chlorfenvinphos in soil between the control plot and those plots receiving chlorfenvinphos annually for 20 years (Table 4), the mean half-life being 26 days. It may be noted that in some other soils,[17,18] repeated applications led to increasingly rapid breakdown of this insecticide. It is not clear why adaptation arises in some circumstances and not in others, but the role of soil pH may be one reason for such differences in behaviour. Nonetheless whatever factors in the Rothamsted soil prevented adaptation to chlorfenvinphos did not inhibit adaptation to aldicarb (see Section 3.3.4).

3.3.2 Benomyl (carbendazim)

Breakdown of carbendazim in the first set of incubations in soil was variable (results not given), compounded by difficulties with the HPLC using the initial, neutral running solvent. In the repeated set of incubations using soil sampled 25 months after the last field applications and using the basic running solvent for HPLC, breakdown was more consistent; the rate constants (Table 4) showed the same pattern as previously and varied over a range of about two-fold. These differences could not be related to the treatment history of the plots nor to soil pH (soil pH values in 0·01 M calcium chloride of 6·22, 6·21 and 6·00 for k values of 0·034, 0·050 and 0·024 day^{-1} respectively). Behaviour over the first 15 days was the main cause of these differences, with a lag phase occurring for the soils from the control and benomyl-treated plots; degradation rates beyond this period were not significantly different amongst the plots and averaged 0·035 day^{-1} i.e. $t_{1/2}$ = 20 days.

3.3.3 Triadimefon

As with chlorfenvinphos, the breakdown of triadimefon was not influenced by the treatment history of the plots. In soil from each of the three plots studied, triadimefon was rapidly reduced ($k_A + k_B \approx 0{\cdot}12\ day^{-1}$, $t_{1/2} \approx 5{\cdot}75$ days) to triadimenol, which exists as two diastereoisomers[19] with the 1*R*,2*S*; 1*S*,2*R* being predominant (Fig. 2) by about three-fold (i.e. $k_A \approx 3\ k_B$). These triadimenol compounds are also fungicidal, and were too persistent in these incubations for accurate assessment of their breakdown rates ($k_D \approx k_E \approx 0{\cdot}002\ day^{-1}$, $t_{1/2} \approx 350$ days); the pattern of triadimenol behaviour was similar in soils from all three plots (Fig. 3(a)).

3.3.4 Aldicarb

The insecticidal/nematicidal activity of aldicarb in soil is due both to parent aldicarb and to its more persistent oxidation products, aldicarb sulfoxide and aldicarb sulfone (aldoxycarb). In contrast to the behaviour of the other pesticides examined, breakdown of the toxic aldicarb compounds in soil (Fig. 4) was greatly influenced by the treatment history, being much faster in soils taken from plots treated repeatedly with aldicarb (Fig. 3(b)).

Transformation of aldicarb itself, occurring primarily by oxidation (k_A) to the sulfoxide and which may be primarily a chemical process in soil, was rapid in all soil samples irrespective of treatment history; the rate of further oxidation to the sulfone (k_B) was also unaffected

TABLE 4
Effect of Treatment History on the Rate of Breakdown in Soil of Chlorfenvinphos and Benomyl

Treatment history (1974–93)	*Rate constant (±SD) (day^{-1})*[a]	
	Chlorfenvinphos	*Benomyl*[b]
Control	0·034 (±0·001)	0·034 (±0·003)
Chlorfenvinphos or benomyl only[c]	0·031 (±0·002)	0·050 (±0·003)
All pesticides, including benomyl and chlorfenvinphos	0·027 (±0·002)	0·024 (±0·003)

[a] Chlorfenvinphos and benomyl were incubated over 81 and 77 days respectively, with 15 sampling times.
[b] Applied and measured as carbendazim.
[c] Breakdown rates reported for the soils receiving 20-year treatment with the respective compound.

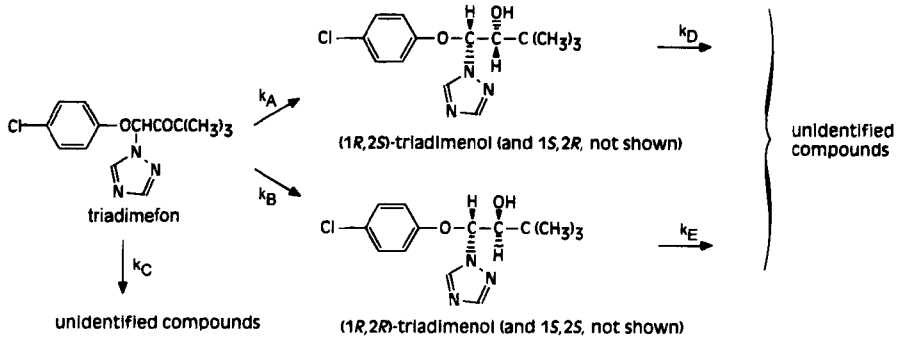

Fig. 2. Breakdown of triadimefon in soil with the rate constants obtained from the MLP analysis.

by the soil history (Table 5). However hydrolysis of the carbamate group from aldicarb sulfoxide (k_D) was on average 18 times faster in soil from the two aldicarb-treated plots under test compared to the control, and hydrolysis of aldicarb sulfone (k_E) was on average six times faster. Thus, in the incubations at 15°C, toxic residues could not be measured after 30 days in the soils receiving the prior aldicarb treatments, whilst these oxidation products of aldicarb persisted beyond 90 days in the control. Behaviour was similar in the plots receiving

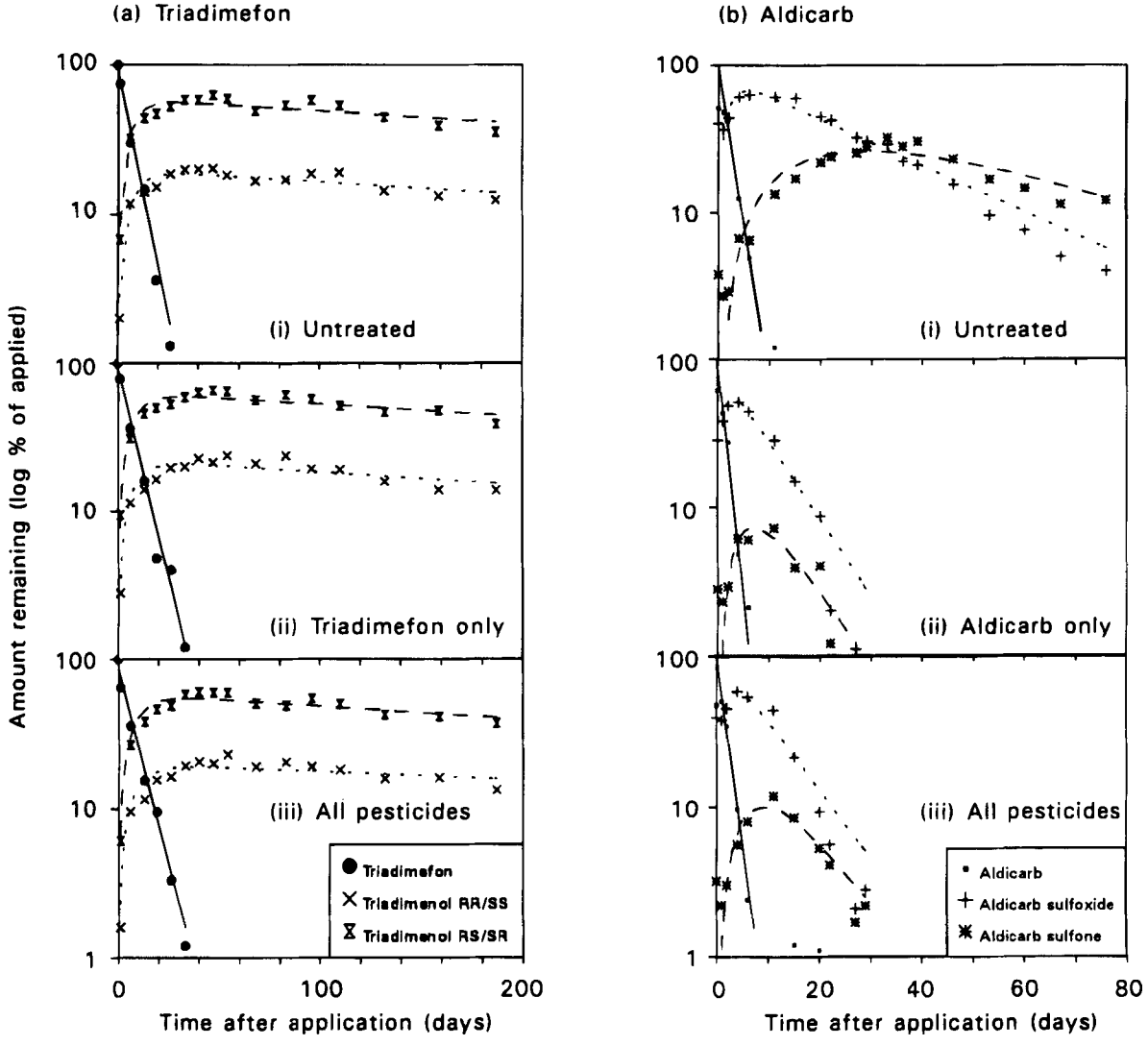

Fig. 3. Influence of treatment history on the breakdown of (a) triadimefon and (b) aldicarb in soils from plots treated repeatedly (i) control plot (ii) plot receiving that compound only (triadimefon for 12 years or aldicarb for 20 years) (iii) plot receiving all five pesticides, including triadimefon and aldicarb.

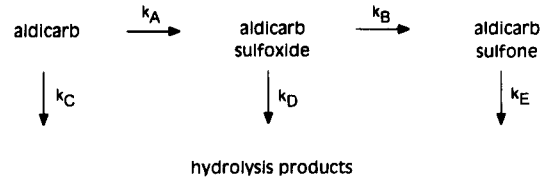

Fig. 4. Breakdown of aldicarb in soil with the rate constants obtained from the MLP analysis.

either aldicarb alone or aldicarb plus the four other pesticides annually since 1974. The lack of effect of treatment history on the transformation of parent aldicarb accorded with similar observations in this[20] and other experiments.[21]

Using soils taken from this experiment on 10 December 1986, Suett & Jukes[20] had previously observed such microbiological adaptation to aldicarb; in their tests the aldicarb residues broke down three times more quickly in soil from aldicarb-treated plots, and so it would seem that the adaptation process has continued since then to give the present larger effects. It should be noted that the plot design was not originally intended to take account of these processes, and the relatively narrow paths might allow soil to be carried on the plough from one plot to the next and so 'seed' the untreated plots including the control; nonetheless, breakdown of aldicarb in the control soil was similar to that reported in other soils with no history of aldicarb usage,[22,23] and so such potential contamination would not seem to have been a significant problem.

4 DISCUSSION

None of the five main pesticide treatments, either singly or in any combination, had a deleterious effect on the yield of spring barley over the 20 years (1974–1993) of the experiment. Indeed aldicarb, except in the later years, gave substantial yield increases by controlling aphids, soil-living nematodes and perhaps soil insects; monitoring in the first decade of the experiment indicated that aldicarb controlled aphids well (results not presented) and the soil sampling in 1991 showed that populations of plant-parasitic nematodes were very low on all the plots receiving aldicarb (Hooper and Iliev, pers. comm.). Yields from these plots in 1994, the first year in which the pesticide treatments were not applied, averaged 5·27 tonne ha^{-1} and did not vary significantly with the treatment history (Bromilow, Evans & Nicholls, unpublished). This is a preliminary indication of there being no residual effects, and also that possible pest and/or disease control by these compounds was not previously masking a decline in soil fertility as assessed by grain yield.

Analysis for the more persistent compounds in soil taken from the plots some 22 or 17 months after the last autumn and spring treatments respectively found no detectable residues, not even for the major diastereoisomer of triadimenol which was rather stable in soil in the laboratory incubations. Such incubations with these soil samples indicated no influence of treatment history on the breakdown of benomyl (as carbendazim), chlorfenvinphos and triadimefon; in contrast, the breakdown of the active oxidation products of aldicarb was greatly enhanced in soil from plots that had received aldicarb repeatedly. Such enhanced breakdown could explain the decline over the years in the yield increases caused by aldicarb treatments. However aldicarb was still greatly depressing the populations of plant-parasitic nematodes in 1991, towards the end of the experiment, but presumably was failing to give such prolonged control as previously of the insect pests.

Hart and Brookes,[24] using topsoil sampled from the plots on 9 April 1992 and on 26 October 1992, i.e. samples taken about four weeks after the spring and autumn pesticide applications respectively, assessed microbial activity in each of the plots. For the spring samples, soil respiration, which averaged 2·6 μg CO_2 carbon g^{-1} soil day^{-1} at 25°C, was not significantly influenced by the pesticide treatments; similarly, there were no significant effects on microbial biomass carbon (overall 166·6 μg g^{-1} soil), measured using the fumigation-extraction method, save that aldicarb treatments slightly but significantly ($P > 0·05$) increased this carbon fraction to 179·1 μg g^{-1} soil. Results for the

TABLE 5
Effect of Treatment History on the Rate of Breakdown in Soil of the Toxic Oxidation Products of Aldicarb

	Rate constants ($\pm SD$) (day^{-1})		
Treatment history (1974–93)	k_B	k_D	k_E
Control	0·033 (±0·003)	0·0035 (±0·0037)	0·038 (±0·005)
Aldicarb only[a]	0·051	0·069	0·27
Aldicarb plus all other pesticides	0·050 (±0.018)	0·055 (±0·021)	0·20 (±0·082)

[a] Standard errors were not obtainable as the data were too variable.

autumn samples were very similar. Though all the plots usually received a post-emergence herbicide spray, the herbicides chosen for this were weakly sorbed and relatively non-persistent acidic compounds; given these properties and that the application was to the growing crop in May/June rather than to the soil, it is considered unlikely that these applications confound the interpretation of the effects of the repeated soil-applied treatments.

This experiment utilised annual soil treatments at typical or slightly high rates of pesticides, several of which are fairly persistent, and as such was designed to maximise the opportunity for any deleterious effects caused by the agricultural use of pesticides to manifest themselves. Nonetheless, no deleterious effects on soil fertility could be seen, either as defined by crop yield or by the activity and populations of micro-organisms. Whilst results from five pesticides should not be taken to be definitive for all the many pesticides in use today, the conclusion that we draw is that there is no evidence from these and other studies that modern pesticides, at permitted application rates and uses, do damage soil fertility even after many years of use.

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